

## RESEARCH ARTICLE

# The influence of environmental drivers on the enrichment of organic carbon in the sea surface microlayer and in submicron aerosol particles – measurements from the Atlantic Ocean

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The export of organic matter from ocean to atmosphere represents a substantial carbon flux in the Earth system, yet the impact of environmental drivers on this transfer is not fully understood. This work presents dissolved and particulate organic carbon (DOC, POC) concentrations, their enrichment factors in the sea surface microlayer (SML), and equivalent measurements in marine aerosol particles across the Atlantic Ocean. DOC concentrations averaged  $161 \pm 139 \mu\text{mol L}^{-1}$  ( $n = 78$ ) in bulk seawater and  $225 \pm 175 \mu\text{mol L}^{-1}$  ( $n = 79$ ) in the SML; POC concentrations averaged  $13 \pm 11 \mu\text{mol L}^{-1}$  ( $n = 80$ ) and  $17 \pm 10 \mu\text{mol L}^{-1}$  ( $n = 80$ ), respectively. High DOC and POC enrichment factors were observed when samples had low concentrations, and lower enrichments when concentrations were high. The impacts of wind speed and chlorophyll-a levels on concentrations and enrichment of DOC and POC in seawater were insignificant. In ambient submicron marine aerosol particles the concentration of water-soluble organic carbon was approximately  $0.2 \mu\text{g m}^{-3}$ . Water-insoluble organic carbon concentrations varied between  $0.01$  and  $0.9 \mu\text{g m}^{-3}$ , with highest concentrations observed when chlorophyll-a concentrations were high. Coordinated measurements of bulk seawater, the SML and aerosol particles enabled calculation of enrichment factors of organic carbon in submicron marine ambient aerosols, which ranged from  $10^3$  to  $10^4$  during periods of low chlorophyll-a concentrations and up to  $10^5$  when chlorophyll-a levels were high. The results suggest that elevated local biological activity enhances the enrichment of marine-sourced organic carbon on aerosol particles. However, implementation of the results in source functions based on wind speed and chlorophyll-a concentrations underestimated the organic fraction at low biological activity by about 30%. There may be additional atmospheric and oceanic parameters to consider for accurately predicting organic fractions on aerosol particles.

**Keywords:** organic carbon; sea surface microlayer; marine aerosol particles; enrichment factor; source function; chlorophyll-a; wind speed

## 1 Introduction

The oceans are a significant source of marine aerosol particles which may impact the radiation budget of the earth directly by scattering and absorbing solar radiation and indirectly by affecting cloud formation processes. Marine aerosol particles are produced at the sea surface primarily due to interaction between wind and waves (bubble bursting) and secondarily by gas-to-particle conversion (secondary organic aerosol, SOA; e.g., de Leeuw

et al. 2014. These naturally produced aerosol particles can then be influenced by various environmental factors. In particular, submicron aerosol particles ( $\text{PM}_{10}$ ) that have an atmospheric lifetime of several days (Madry et al., 2011) may be affected as a result of processing in the atmosphere and by anthropogenic impacts. Frossard et al. (2014) measured significant contributions of continental sources and ship pollution to aerosol particles sampled in different regions of the Atlantic and Pacific Ocean. In other regions (North Atlantic and Arctic Ocean), however, these authors could identify the aerosol particles as largely marine in nature. Using isotopic carbon analysis, Ceburnis et al. (2011) found a strong marine organic aerosol source in the North Atlantic under bloom conditions and showed that over 80% of the detected carbon originated directly from plankton emissions. Recently, Miyazaki et al. (2016)

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identified a significant contribution of oceanic dissolved organic carbon to submicron particles in the marine boundary layer, regardless of the oceanic area. They demonstrated that water soluble organic carbon in seawater is closely linked with the submicron water soluble organic carbon on aerosol particles. McCoy et al. (2015) reported that natural aerosol particles are linked to seasonal and spatial patterns of Southern Ocean cloud albedo. In conclusion, despite possible anthropogenic influences, naturally produced aerosol particles may play a dominant role in the remote marine boundary layer, depending on the region and meteorological condition.

The chemical composition of aerosol particles determines their role in cloud processes. Research of the last two decades has shown that marine aerosol particles contain a large quantity of organic material (e.g., Quinn and Bates, 2011, and references therein). As enrichment increases with particle size (O'Dowd et al., 2004), the sub-micrometer aerosol particles that play a critical role in the formation of cloud condensation nuclei are often dominated by organic matter (OM) (Quinn and Bates, 2011). Yet, the environmental drivers and mechanisms for the OM enrichment are not very clear. Biological activity in the surface ocean has been suggested to be one important parameter. Concentrations of marine organic aerosols were found to be dependent on seasonal cycles of phytoplankton activity as reflected in correlations between chlorophyll-a (chl-a) and organic aerosol mass (O'Dowd et al., 2004; Facchini et al., 2008a; Ovadnevaite et al., 2011; Rinaldi et al., 2013; Schwier et al., 2015). On the other hand, there are several studies in which a direct link between chl-a concentration and organic matter on aerosol particles could not be detected. For example, Quinn et al. (2014) suggested that the high reservoir of dissolved organic carbon in the ocean is responsible for the organic enrichment in freshly emitted sea spray aerosol, thus dominating over any influence of recent local biological activity based on chlorophyll concentrations. In a mesocosm experiment, a negative correlation between organic particles (of a specific size range) and chl-a was identified, although a positive correlation between these particles and bacterial abundance was observed (Prather et al., 2013). These authors concluded that the response of aerosol composition and its mixing state to changes in seawater is size-dependent. Such findings demonstrate the high variability of characteristics observed in organic aerosol particles in the marine environment, while also reflecting the limitations of current knowledge on the effects of biogeochemical drivers on marine aerosol particle organic composition.

When regarding the upwards export of organic material from the oceans, not only the bulk ocean water has to be considered, but also the sea surface microlayer (SML), representing the uppermost layer of the ocean and therefore the interface for all gaseous, liquid and particulate mass transfer processes between the ocean and the atmosphere (Cunliffe et al., 2013). The SML has often been reported to be enriched with both inorganic and organic matter (e.g., Liss and Duce, 1997; Wurl et al., 2011b; Engel and Galgani, 2016) and to enable interfacial photochemical processes

leading to the production of important aerosol precursors such as volatile organic compounds (Liss and Duce, 1997; Ciuraru et al., 2015). Specific organic compound groups (e.g., gel-like organic material) originating from the SML have been detected on submicron aerosol particles. These biopolymers are understood to influence the cloud condensation and ice nucleating properties of the particles (Matrai et al., 2008; Orellana et al., 2011; Wilson et al., 2015). Russell et al. (2010) have demonstrated that the enrichment of OM in the submicron marine aerosol particles is several orders of magnitude higher than OM enrichment measured in the SML (in comparison to bulk seawater).

In a conceptual relationship Gantt et al. (2011) proposed that, besides aerosol size, wind speed and biological activity (as reflected in chl-a concentrations) are the most important parameters regulating the organic matter content of primary aerosol particles (particles that are generated at the ocean surface, often referred to as sea spray aerosol or SSA). Based on this model it is predicted that highest organic enrichment in SSA particles occurs at low wind conditions when marine aerosol production is minimal and the SML covers the ocean surface. At higher wind speeds the sea spray production is increased; however, the organic matter in the sea spray aerosol ( $OM_{SSA}$ ) is reduced due to the stronger mixing of the SML with bulk seawater and the consequently smaller SML coverage. Rinaldi et al. (2013) confirmed an inverse correlation between the organic aerosol fraction and wind speed and presented a function of  $OM_{SSA}$  including wind speed and chl-a as driving factors from a two-dimensional regression analysis. In the context of the depicted source function the best fit was obtained using chl-a data with a time resolution of about one week, thus averaging over fast temporal changes.

Despite the progress in parameterizations, currently there are few comprehensive field studies on organic matter in the marine environment that take into account biogeochemical parameters in order to understand processes and to evaluate and develop concepts outlining air-sea exchange of organic matter, especially involving the SML.

In this study, measurements of organic carbon in seawater (both in the SML and the bulk water), as well as in submicron marine aerosol particles, were conducted as concerted measurements throughout different regions of the Atlantic Ocean. A large dataset was obtained during various field campaigns covering large parts of the Atlantic Ocean. Specifically, concentrations of dissolved organic carbon (DOC) and particulate organic carbon (POC) both in seawater and in the SML, as well as water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WISOC) in the submicron aerosol particles, were determined. Enrichment factors of organic carbon in the submicron aerosol particles ( $EF_{aer}$ ) were calculated, representing the first  $EF_{aer}$  for ambient marine aerosol particles based on simultaneous measurements. In order to investigate the influence of biogeochemical parameters, the organic carbon concentrations (in the SML, bulk water and aerosol particles) were analyzed as functions of chl-a concentration and wind speed to determine if and

to what extent wind stress and biological activity in the surface ocean have an impact on the concentration and enrichment of organic carbon in the marine environment. Finally, the WISOC results were applied to existing (Rinaldi et al., 2013), as well as newly developed, source functions based on chl-a concentration and wind speed.

## 2 Experimental

### 2.1 Sampling areas

The sampling regions for the present study were located in the tropical and the temperate climate zones of the Atlantic Ocean (**Table 1, Figure 1**). Samples were taken during campaigns conducted at the Cape Verde Atmospheric Observatory (CVAO), a remote marine station described in Carpenter et al. (2010) and Fomba et al. (2014) during May 2011 and November 2011 and 2013. Samples were also taken at the location of Raune Fjord in Bergen, Norway, following a spring bloom during

May–June 2011, as well as during two transects with the RV *Polarstern* from Punta Arenas, Chile, to Bremerhaven (ANT-XXVIII/5) during spring 2012 and from Cape Town to Bremerhaven (ANT-XXIX/10) during spring 2014. Within these two transects regions in the tropical climate zone (CVAO) and the temperate climate zone (Bergen), as well as a large part of the Atlantic Ocean, are covered.

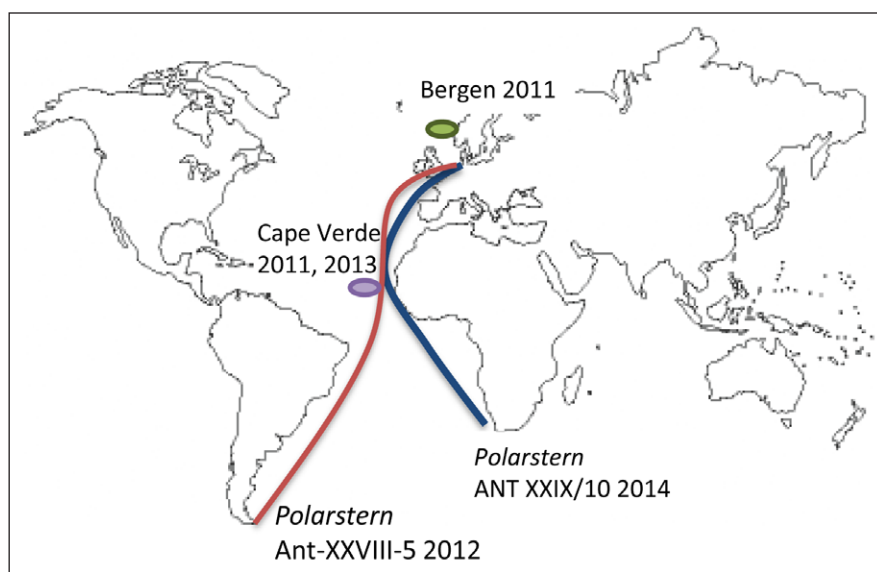
#### 2.1.1 Aerosol particle sampling

A high volume Digital sampler DHA-80 (Walter Riemer Messtechnik, Germany) was used for aerosol particle sampling. At the CVAO measurement station, the aerosol sampler was installed at a height of 30 m on top of a tower located directly at the seaside. During the Bergen campaign, the aerosol sampler was placed on a hill, at a height of approximately 10 m, facing the Fjord. During the *Polarstern* cruises, the sampler was mounted on top of the observation deck at a height of approximately

**Table 1:** Details of the sampling campaigns included in this study. DOI: <https://doi.org/10.1525/elementa.225.t1>

Campaign	Sampling area		Sampling date	No. of paired samples of SML <sup>a</sup> + bulk seawater	No. of marine aerosol samples (filters)
Cape Verde SOPRAN 2011-I	North Atlantic (tropical zone)	offshore	May 2011	6	6
Cape Verde SOPRAN 2011-II	North Atlantic (tropical zone)	offshore	November 2011	15	7
Cape Verde SOPRAN 2013	North Atlantic (tropical zone)	offshore/ onshore	November 2013	11	8
Bergen 2011	North Atlantic	onshore	May–June 2011	10	15
<i>Polarstern</i> ANT-XXVIII/5 2012	North–South Atlantic (transect)	offshore	April–May 2012	22	20
<i>Polarstern</i> ANT-XXIX/10 2014	North/South Atlantic (transect)	offshore	March–April 2014	17	8

<sup>a</sup> Sea surface microlayer.



**Figure 1:** Illustration of generalized cruise tracks of the different campaigns included in this study. DOI: <https://doi.org/10.1525/elementa.225.f1>

30 m. Submicron aerosol particles ( $PM_{10}$ ) were collected on preheated 150 mm quartz fiber filters (Munktell, MK 360) at a flow rate of  $500\text{ L min}^{-1}$ . A sampling time of approximately 24 hours, from midnight to midnight (UTC), was applied. Following the sampling, filters were stored in aluminum boxes that were kept in a freezer at  $-20\text{ }^{\circ}\text{C}$ . At the end of the campaigns, the samples were transported on dry ice to the laboratories located in the TROPOS Institute, Leipzig.

### 2.1.2 Water sampling: SML and bulk water

At the CVAO, the water samples were taken by use of a fishing boat either in front of the station (onshore samples) or within a distance of at least 5 km from the station (offshore samples). During the *Polarstern* campaigns, water sampling was performed using a rubber boat that was launched from the vessel; samples were taken beyond a distance of approximately 500 m from the vessel in order to avoid contamination. In Bergen, the samples were taken in the Fjord from a rubber boat while at a maximum distance of 500 m to the coast (onshore samples).

For SML sampling, the glass plate technique as one typical SML sampling strategy was applied (Cunliffe and Wurl, 2014). A glass plate with a sampling area of  $2000\text{ cm}^2$  was vertically immersed into the water and then slowly drawn upwards. The surface film adheres to the surface of the glass and is removed using framed Teflon wipers (Stolle et al., 2010; van Pinxteren et al., 2012). Great care was taken to ensure that during all field campaigns a uniform withdrawal rate of approximately  $10\text{ cm s}^{-1}$  was applied. Bulk seawater was collected from a depth of 1 m using a specially designed device consisting of a glass bottle mounted on a telescopic rod used to monitor sampling depth. The bottle was opened underwater at the intended sampling depth with a specifically conceived seal-opener.

A portion of each water sample was filtered over Whatman GF-F filters (pore size:  $0.7\text{ }\mu\text{m}$ ) for POC analysis. Also, additional bulk water samples were taken at each sampling day and filtered over Whatman GF-F filters for chl-a analysis (volumes of  $0.5\text{--}5\text{ L}$ ). All water samples were stored in glass bottles at  $-20\text{ }^{\circ}\text{C}$  until the time of analysis. Following each sampling procedure, all materials were cleaned extensively using reagent water.

Blank samples were collected at the beginning, middle and end of the campaign during all campaigns. To this end, reagent water was loaded into bottles (the same kind used for the purpose of bulk water/SML sampling), which were taken to the field and subjected to the same procedures applied to the field samples, such as filtering and freezing. Blank values were generally lower than 10% of the DOC and POC concentrations values identified in the field samples. Average blank values were subtracted from the measured DOC and POC concentrations.

## 2.2 Analytics

### 2.2.1 Aerosol particle filter analytics

Prior to their application, aerosol filters were preheated at a temperature of  $105\text{ }^{\circ}\text{C}$  for a duration of 24 hours. Organic carbon (OC) and elemental carbon (EC) determination was carried out by means of a thermal-optical method using the

Sunset Laboratory Dual-Optical Carbonaceous Analyzer (Sunset Laboratory Inc., U.S.A.) from a filter piece with an area of  $1.5\text{ cm}^2$ . The EUSAAR 2 temperature protocol was utilized, and a charring correction was applied (Cavalli et al., 2010). The correction value for pyrolytic carbon was determined based on measurements of a sample transmission using a  $678\text{ nm}$  laser. Samples were thermally desorbed from the filter medium under an inert He-atmosphere followed by an oxidizing  $\text{O}_2/\text{He}$ -atmosphere while applying carefully controlled heating ramps. A flame ionization detector was used to quantify methane following a catalytic methanation of  $\text{CO}_2$ .

The WSOC content of the collected aerosol samples was measured by analyzing filtered aqueous particle extract (from a filter piece of approximately  $21\text{ cm}^2$  extracted in  $25\text{ mL}$  water) using a  $0.45\text{ }\mu\text{m}$  syringe filter and, subsequently, a TOC-VCPH analyzer (Shimadzu, Japan). To convert inorganic carbonates to carbon dioxide ( $\text{CO}_2$ ),  $1.5\text{ vol\%}$  of a hydrochloric acid solution ( $2\text{ M}$ ) was added to the aqueous extract, resulting in a pH value of 2. Afterwards, synthetic particle-free air was channeled through the acidified sample in order to remove the formed  $\text{CO}_2$ . The oxidation of the carbon present within the sample was induced by adding  $300\text{ }\mu\text{L}$  of the carbonate-free solutions to a catalyst (aluminum oxide/platinum on quartz wool) maintained at a temperature of  $720\text{ }^{\circ}\text{C}$ . The formed carbon dioxide was analyzed by means of non-dispersive infrared (NDIR) detection. For quantification, an external calibration with potassium hydrogen phthalate was applied. WSOC concentrations were calculated as the difference between OC and WSOC (Cavalli et al., 2004).

Concentrations of sodium and other inorganic ions (chloride, sulfate, nitrate, ammonium, potassium, magnesium, calcium) in filtered ( $0.45\text{ }\mu\text{m}$  syringe filter) aqueous extracts (25% of the filter in  $30\text{ mL}$  of water) were determined using ion chromatography (ICS3000, Dionex, Sunnyvale, CA, USA), as described by Müller et al., (2010).

Field blanks were obtained by inserting the filters into the Digitel sampler for a duration of 24 hours without loading them. Three field blanks were collected during the course of each campaign. The mean values of the obtained blanks were subtracted from the WSOC concentrations and OC concentrations, whereas sodium blanks always fell below the detection limit.

### 2.2.2 Seawater analytics

For seawater DOC, the organic carbon was quantified in filtered seawater (GF-F Whatman filters) using the TOC-VCPH analyzer (Shimadzu, Japan), the same instrument applied to aerosol particles. Repetitive analysis of frozen samples revealed that no artifacts were caused as a result of freezing and storing procedures, as the values of the re-analyzed samples showed relative standard deviations below 10%.

For the purpose of POC analysis, different quantities of seawater were filtered over preheated Whatman GF-F filters kept at  $450\text{ }^{\circ}\text{C}$  for 5 hours, following the procedure reported by Taucher et al. (2012). From these filters, POC concentrations were measured directly by applying a two-step thermographic method using a commercial carbon



analyzer C-mat 5500 (Ströhlein, Germany). The applied method is a variation of the method described in the VDI Guideline (VDI 2465, Part 2) issued in Germany. As a first step, nitrogen was employed to act as a carrier gas, kept at a temperature of 650 °C, for the purpose of OC volatilization. Furthermore, as a second step, EC was combusted at a temperature of 650 °C in an oxygen atmosphere. The EUSAAR 2 temperature protocol could not be applied, as the final temperature (850 °C) would have caused the GF-F filters to melt.

Salinity in the SML and the bulk water was measured occasionally, using a refractometer (OCS.tec GmbH & Co. KG, Neuching, Germany). The detected salinities varied between 35 and 39 ppt (formerly given as PSU) in all investigated regions.

### 2.2.3 Back trajectories and wind speed

Information regarding the origins of air masses was obtained on the basis of back trajectory analyses. Seven-day back trajectories were calculated on an hourly basis within the sampling intervals, using the NOAA HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, <http://www.arl.noaa.gov/ready/hysplit4.html>, 26.11.16) in the ensemble mode at an arrival height of 500 m  $\pm$  200 m (van Pinxteren et al., 2010).

The wind speeds reported here represent either the averaged wind speed over the aerosol sampling period (typically 24 hours) or the wind speed at the sampling time in case of seawater sample collection. The wind speed values were achieved on the basis of on-board measurements during the *Polarstern* cruises (König-Langlo, 2012; König-Langlo, 2014) and from local weather stations at the CVAO and the Bergen campaign. The registered values were converted to a uniform wind speed at a height of 10 m according to Equation 1 provided by Kleemann and Meli (1993):

$$v_h = v_{10} \left( \frac{h}{10} \right)^g \quad (1)$$

where  $v_h$  indicates wind speed at the measured height while  $v_{10}$  indicates the wind speed at a height of 10 m. For open areas such as oceans or deserts, the exponent  $g$  is set to 0.16 (Kleemann and Meli, 1993). Wurl et al. (2011b) have categorized the wind speeds into three groups: low (0–2 m s<sup>−1</sup>, referring to state 0), moderate (2–5 m s<sup>−1</sup>, referring to states 1–2) and high (5–10 m s<sup>−1</sup>, referring to states above 2.5) conditions according to Pierson and Moskowitz (1964). The data obtained in the present study consistently showed wind speeds at higher than 2 m s<sup>−1</sup>. Therefore, we slightly modified the respective ranges suggested by Wurl et al. (2011b) and classified our data into two categories designating either “low wind”, at values ranging between 2 and 5 m s<sup>−1</sup>, or “high wind” conditions at wind speeds of higher than 5 m s<sup>−1</sup>.

### 2.2.4 Chlorophyll-a (Chl-a)

Chl-a is a regularly applied and well accessible indicator for the purpose of describing biological activity of the surface ocean (O'Dowd et al., 2004; de Leeuw et al., 2011). Chl-a values may be derived from satellite retrievals or

directly from seawater measurements. For this study, chl-a concentrations were measured by means of HPLC and fluorescence detection (Dionex, Sunnyvale, CA, USA). GF-F filters were extracted in 5 mL ethanol, and 20 µL of the extract were injected into the HPLC system under gradient elution using methanol/acetonitrile/water systems as eluents. Chl-a concentrations were also obtained from satellite retrievals provided by the Ocean Color Web operated by the NASA (<http://oceancolor.gsfc.nasa.gov/>, 26.07.16). The concentrations were obtained using MODIS-AQUA and MODIS-TERRA within a radius of 1° from the sampling location and then averaged based on results from both instruments in order to fill data gaps due to cloud coverage. The resulting values from both approaches were categorized into “low chl-a” for chl-a values between 0.1 and 0.6 µg L<sup>−1</sup> or “high chl-a” for values starting at 0.9 µg L<sup>−1</sup>. Chl-a concentration values below the detection limit were set to the detection limit value and classified as within the “low chl-a” category.

### 2.2.5 Data analysis

The enrichment factor (EF) in the SML was calculated by dividing the concentration ( $c$ ) of DOC or POC in the SML by the respective concentration measured in the bulk water (BW) using the following equations:

$$EF_{SML}(DOC) = \frac{c \text{ DOC}(SML)}{c \text{ DOC}(BW)} \quad (2)$$

$$EF_{SML}(POC) = \frac{c \text{ POC}(SML)}{c \text{ POC}(BW)} \quad (3)$$

Enrichment of DOC and POC in the SML is indicated by  $EF > 1$ , while depletion is indicated by  $EF < 1$ .

The thickness of the SML ( $D_f$ ) was determined based on the quotient between the sampled volume of the SML and the sampling area of the glass plate:

$$D_f \text{ (cm)} = \frac{V(\text{cm}^3)}{A(\text{cm}^2)} \quad (4)$$

In order to calculate the enrichment factors for the organic carbon on submicron aerosol particles, the WSOC (on aerosol particles) was assigned to DOC (in seawater) and the WISOC (on aerosol particles) was assigned to POC (in seawater). The abbreviations  $EF_{aer}(DOC)$  and  $EF_{aer}(POC)$  were applied uniformly:

$$EF_{aer}(DOC) = \frac{WSOC/Na^+(aer)}{DOC(SML)/Na^+(SML)} \quad (5)$$

$$EF_{aer}(POC) = \frac{WISOC/Na^+(aer)}{POC(SML)/Na^+(SML)} \quad (6)$$

The  $EF_{aer}$  values were calculated combining the data points sampled on a daily basis. To this end, aerosol concentrations, typically sampled at a 24-hour interval, were combined with SML concentrations (spot samples) that had been collected in the middle of the aerosol sampling

period. During the Bergen campaign, however, the aerosol sampling did not occur simultaneously with the water sampling, as the aerosol filters collected during SML sampling did not meet the criterion of clean marine air (i.e., low EC concentrations, air masses of marine origin, similar and overall low concentrations of inorganic ions across campaigns; more details can be found in Section 3.2). Therefore, for the Bergen campaign, aerosol and SML concentrations were clustered according to the respective chl-*a* and wind speed categories. Subsequently, median DOC and POC concentrations as well as median WSOC, WISOC and sodium concentrations were calculated to then determine  $EF_{aer}$  (DOC) and  $EF_{aer}$  (POC) according to Equations 5 and 6.

According to the applied analytical standard protocol, the separation of WSOC/DOC and WISOC/POC is obtained via filtering. As previously described, filters with a pore size of 0.7  $\mu\text{m}$  are utilized routinely for DOC analysis of seawater (GF-F glass fiber filter, Whatman). However, in order to separate WSOC and WISOC in aerosol particle analysis, pore sizes of 0.45  $\mu\text{m}$  are applied as a standard procedure, which is necessary in order to be able to compare data with values reported in the literature. The usage of different filter sizes may cause a higher ratio of DOC to POC compared to the ratio of WSOC to WISOC.

A Pearson correlation matrix was compiled for all data (XLSTAT software). To this end, a Box-Cox transformation of the data was applied when necessary to reduce skewness in the variables. Also, T-tests were performed to test statistical significance using the analysis of variance (ANOVA). Finally, two-dimensional regression approaches were calculated using the software MATLAB.

### 3 Results and discussion

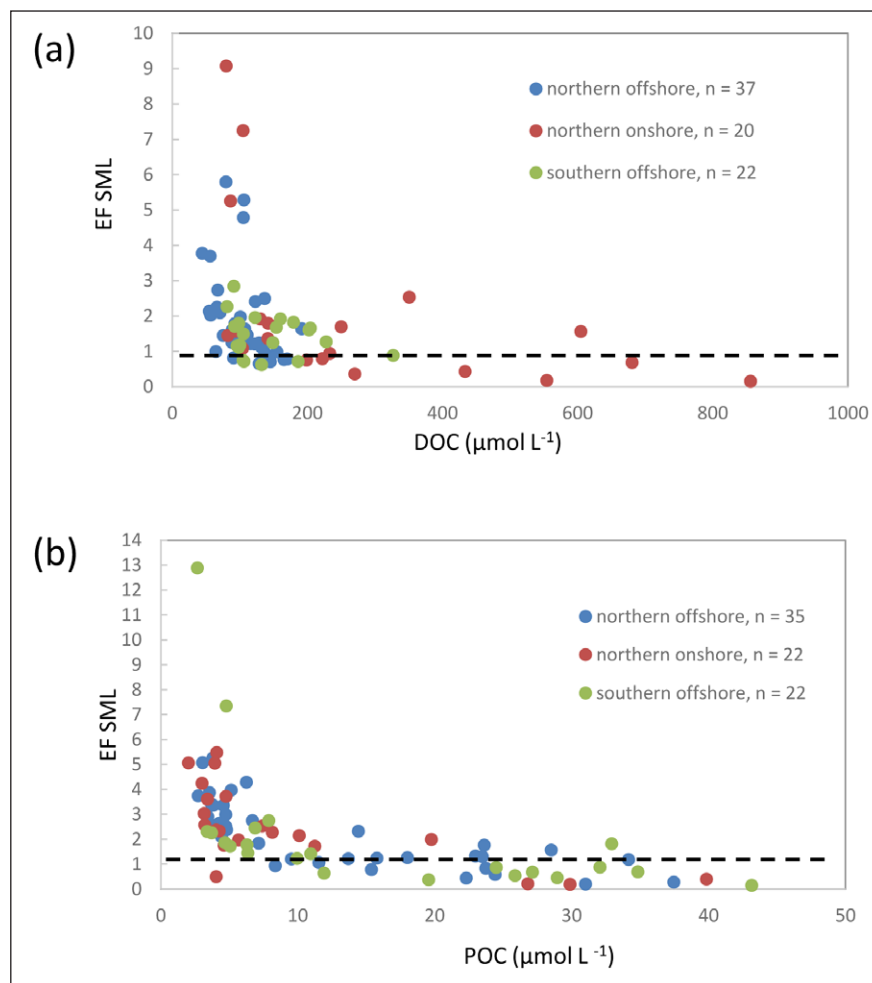
#### 3.1 Seawater

##### 3.1.1 Overview of concentration and enrichment of DOC and POC in seawater and the SML

The measured concentrations of DOC averaged  $161 \pm 139$  (standard deviation, SD;  $n = 78$ ) with a median value of  $122 \mu\text{mol L}^{-1}$  in bulk seawater, and averaged  $225 \pm 175$  ( $n = 79$ ) with a median value of  $164 \mu\text{mol L}^{-1}$  in the SML (for the complete data set see Table S1). These concentration values lie within the range of DOC concentrations for coastal and open ocean water samples reported in the literature (e.g., Carlson, 1983; Mostofa et al., 2013). DOC concentrations in the SML differed significantly from DOC concentrations in bulk water (ANOVA, oneway,  $p = 0.024$  at a 0.05 level). POC concentrations averaged  $13 \pm 11 \mu\text{mol L}^{-1}$  ( $n = 80$ ) (median:  $7.4 \mu\text{mol L}^{-1}$ ) in bulk water, and  $17 \pm 10 \mu\text{mol L}^{-1}$  ( $n = 80$ ) (median:  $13.2 \mu\text{mol L}^{-1}$ ) in the SML. POC concentrations in the SML also differed significantly from bulk water concentrations ( $p = 0.029$ ). Romankevich (1984) summarized the results of POC measurements obtained in a number of studies and found average POC concentrations in the Atlantic Ocean to be approximately  $5 \mu\text{mol L}^{-1}$ , with maximum values up to  $52 \mu\text{mol L}^{-1}$ . However, in most of the studies presented by Romankevich (1984), GF-C filters with a pore size of 1.2  $\mu\text{m}$  were applied for the purpose of POC analysis. In the present study we applied GF-F filters with a pore size of

0.7  $\mu\text{m}$  in accordance with the Practical Guidelines for the Analysis of Seawater (Wurl, 2009). GF-F filters are the classical filter material due to ease of cleaning and low blanks (Wurl, 2009). The smaller pore size applied in the present study might explain the slightly higher average POC values when compared to Romankevich (1984), as a larger amount of POC is retained on the filters. Overall differences in analytical protocols and determination methods applied during DOC and POC analysis need to be taken into account when comparing DOC and POC concentrations to literature values. The average enrichment of POC in the SML is slightly higher ( $EF = 2.3 \pm 1.9$ ,  $n = 76$ ) than enrichment of DOC ( $EF = 1.8 \pm 1.5$ ,  $n = 75$ ).

There were no clear patterns observable between wind speed and SML enrichment or concentration of DOC or POC. Had particular subgroups of DOC and POC been measured, they might have shown a different enrichment behavior depending on wind stress. For example, surfactants are consistently enriched in the SML at wind speeds above  $5 \text{ m s}^{-1}$  (Wurl et al., 2011b), while carbohydrates and gel-particles show depletion in the SML and their concentrations often correlate negatively with wind speed (Wurl et al., 2011a, and references therein). Rather than a consistent enrichment of DOC or POC in the SML, our data sets indicate that high enrichment generally occurs when bulk water samples have low DOC concentrations, while low to no enrichment (or even depletion) is observed when bulk water samples have high DOC concentrations (**Figure 2a**). This observation is confirmed by the negative Pearson coefficient ( $-0.60$ ) determined for bulk water concentration and enrichment factor (**Table 2**). It seems to be a general trend within various data sets, as summarized by Burrows et al. (2014), and is consistent with a surface saturation effect. At higher bulk water concentrations, there are more molecules competing for a smaller available surface area (Burrows et al., 2014). Lower DOC concentrations are typically observed in open ocean waters, whereas coastal seawaters contain a higher amount as well as a higher variance in DOC concentrations, partly as a result of terrestrial inputs (Mostofa et al., 2013). DOC concentrations determined in the present study are consistent with this regional difference: generally lower concentrations were observed in the open ocean while higher concentrations were detected in onshore regions (**Figure 2a**). These findings are also in agreement with a study conducted by Carlson (1983), who reported DOC as often enriched in the SML, while differences between DOC concentrations measured in SML and bulk water were said to be generally small. He concluded that differences in enrichment between coastal and oceanic samples may reflect differences in microlayer accumulation and removal processes depending on the region. For POC concentrations in this study, the same patterns were observed as for DOC; i.e., high enrichment at low bulk water concentrations and vice versa (Pearson coefficient of  $-0.8$ ; **Table 2**). However, unlike the case for DOC – where low concentrations were mainly found in oceanic samples – low POC concentrations also occurred in coastal samples, and high POC concentrations in oceanic samples (**Figure 2b**). We conclude that POC is more



**Figure 2: Bulk water concentrations versus enrichment.** Bulk water concentrations of DOC (a) and POC (b) versus the enrichment in the SML ( $EF_{SML}$ ) grouped according to different sampling regions. The dashed line represents an enrichment factor of one. DOI: <https://doi.org/10.1525/elementa.225.f2>

evenly distributed among oceanic and coastal water than is DOC.

### 3.1.2 Concentration and enrichment of DOC and POC in relation to wind and chl-a conditions

As a next step, the DOC and POC concentrations were divided into four groups according to their chl-a and wind speed profile, because biological activity and wind speed have been suggested to be two important drivers for the concentration and enrichment of organic carbon into sea spray aerosol (Gantt et al., 2011). The results of a comparison between measured and satellite-derived chl-a concentrations (for details see Section 2.2.4) revealed a reasonably good correlation between the two approaches ( $R^2 = 0.62$ , slope: 0.39, intercept: 0.08; Figure S1). Both datasets show the same trend of highly elevated chl-a levels during the Bergen campaign. However, measured values and satellite values do not agree at times, and the measured values are generally higher than those derived from satellite data. This difference has to be taken into account when evaluating the single campaigns in detail. Both of these chl-a approaches have their limitations; i.e., satellite data are sensitive to cloud coverage, and the measured values represent single spot samples. A diurnal variation of chl-a

was also visible in our data; i.e., when chl-a samples were taken twice a day, the afternoon values were mostly higher (by about 30%) than those observed in the morning. We cannot account for such variations here, as usually only one data point per day was obtained; however, sample collection was generally performed around midday. As only a limited number of chl-a values based on satellite retrievals were available for some campaigns (e.g., only two values could be obtained for the Bergen campaign for the time span of aerosol sampling; see Table S2), the measured chl-a values were applied consistently in the subsequent analyses of this work.

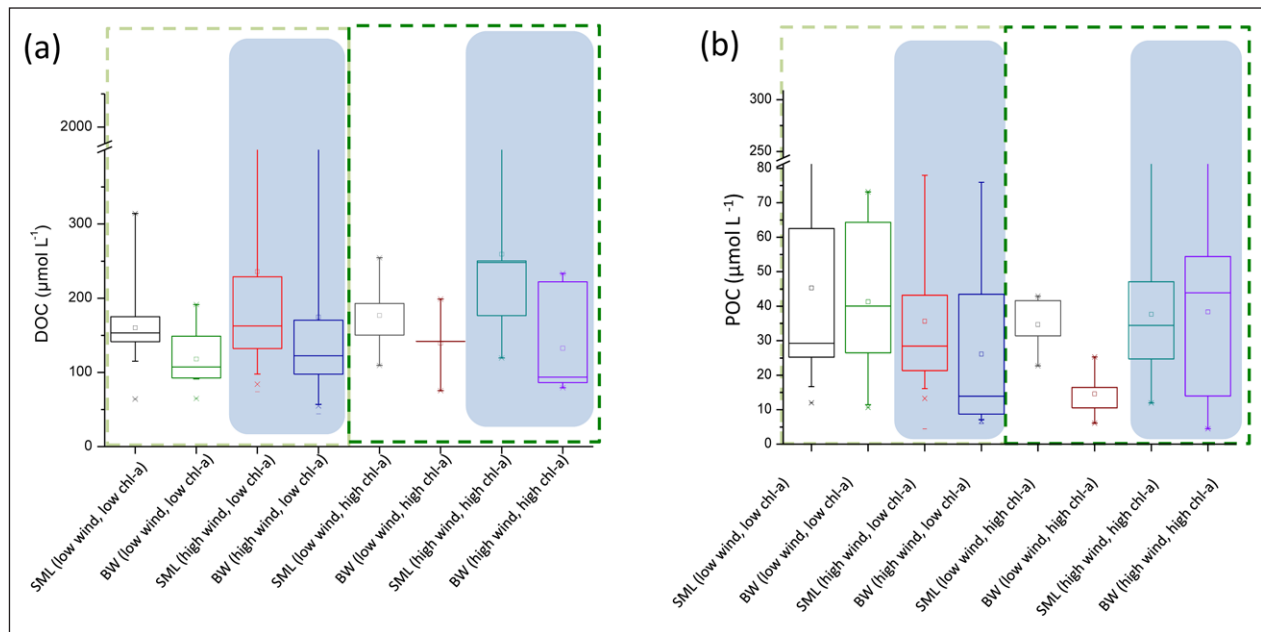
Box plots of the DOC and POC concentrations are shown in Figure 3, and summary statistics of the data (medians, means, maxima and minima) are presented in Table 3. Most of the data can be seen (Figure 3) to lie within the category “high wind and low chl-a” ( $n = 56$ ), followed by “low wind and low chl-a” ( $n = 11$ ). During the Bergen campaign, which was conducted during a bloom period, chl-a was significantly elevated (about  $1 \mu\text{g L}^{-1}$ ); the Bergen data can be referred to as encompassing both of the categories, “high wind and high chl-a” ( $n = 8$ ) and “low wind and high chl-a” ( $n = 4$ ). DOC concentrations detected in the SML and in bulk water did not differ significantly at low chl-a concentrations.

**Table 2:** Pearson correlation matrix on Box-Cox transformed data. <sup>a</sup> DOI: <https://doi.org/10.1525/elementa.225.t2>

Variables <sup>b</sup>	DOC BW	DOC SML	POC BW	POC SML	EF <sub>SML</sub> (DOC)	EF <sub>SML</sub> (POC)	D <sub>f</sub>	WSOC	WISOC	EC	Sodium	Chl-a	Wind speed	EF <sub>aer</sub> (DOC)	EF <sub>aer</sub> (POC)	SST
DOC BW	<b>1</b>	0.271	0.094	-0.147	<b>-0.595</b>	-0.143	0.089	-0.195	0.370	0.062	-0.017	0.029	0.061	-0.149	0.465	0.235
DOC SML		<b>1</b>	-0.053	0.165	0.499	0.162	0.192	-0.242	0.383	0.146	0.090	0.049	0.072	-0.423	0.286	0.179
POC BW			<b>1</b>	0.103	-0.121	<b>-0.813</b>	0.128	0.264	0.074	0.018	-0.082	0.112	-0.043	0.194	0.106	0.020
POC SML				<b>1</b>	0.231	0.358	0.137	-0.002	-0.065	-0.034	-0.084	0.132	-0.113	0.034	-0.262	-0.047
EF <sub>SML</sub> (DOC)					<b>1</b>	0.261	-0.011	-0.141	0.023	0.014	0.165	0.023	0.036	-0.324	-0.157	-0.048
EF <sub>SML</sub> (POC)						<b>1</b>	-0.033	-0.250	-0.177	-0.064	0.032	0.017	-0.067	-0.165	-0.261	-0.051
D <sub>f</sub>							<b>1</b>	0.038	<b>0.606</b>	0.094	-0.172	<b>0.610</b>	-0.099	0.063	0.280	-0.332
WSOC								<b>1</b>	-0.256	0.106	-0.059	-0.025	-0.352	0.543	-0.093	-0.305
WISOC									<b>0.606</b>	0.465	0.087	<b>0.643</b>	0.055	-0.319	<b>0.780</b>	0.370
EC										<b>1</b>	0.166	0.155	-0.063	-0.171	0.206	0.078
Sodium											<b>1</b>	0.304	0.152	<b>-0.780</b>	-0.131	-0.239
Chl-a												<b>1</b>	0.081	-0.227	0.221	<b>-0.589</b>
Wind speed													<b>1</b>	-0.338	0.115	-0.038
EF <sub>aer</sub> (DOC)														<b>1</b>	-0.069	-0.054
EF <sub>aer</sub> (POC)															<b>1</b>	0.320
SST																<b>1</b>

<sup>a</sup> Pearson coefficients higher than 0.6 in bold.<sup>b</sup> BW = bulk seawater, SML = sea surface microlayer, EF = enrichment factor, D<sub>f</sub> = thickness of SML, WSOC = water-soluble organic carbon, WISOC = water-insoluble organic carbon, EC = elemental carbon, aer = aerosol particles, SST = sea surface temperature.





**Figure 3: Concentrations of DOC and POC.** Box and whisker plot of the concentrations of DOC (a) and POC (b) found in SML and bulk water. Each box encloses 50% of the data, the mean value is represented as an open square and the median value as a line. The bottom of the box marks the 25% limit of the data, while the top marks the 75% limit. The lines extending from the top and bottom of each box are the 5% and 95% percentiles within the data set, while the asterisks indicate the data points lying outside of this range (“outliers”). Boxes are color-coded to indicate paired samplings of DOC and POC. The light green dashed lines encompass data from locations with low chl-a concentrations; the dark green dashed lines, those from locations with high chl-a concentrations. The solid blue fields highlight data from locations with high wind speeds. DOI: <https://doi.org/10.1525/elementa.225.f3>

**Table 3: Concentrations of dissolved and particulate organic carbon (DOC, POC) in the sea surface microlayer (SML) and in bulk water (BW) and their enrichment factors in the SML ( $EF_{SML}$ ) according to different wind speed and chl-a categories.** DOI: <https://doi.org/10.1525/elementa.225.t3>

Statistic	DOC ( $\mu\text{mol L}^{-1}$ ) in SML				DOC ( $\mu\text{mol L}^{-1}$ ) in BW			
median	153	163	177	234	107	122	140	94.0
mean	164	240	172	258	118	173	142	131
max	314	946	255	459	192	856	199	233
min	64.1	74.0	109	120	64.8	44.4	75.5	79.5
n	11	56	4	8	11	56	4	7
Statistic	POC ( $\mu\text{mol L}^{-1}$ ) in SML				POC ( $\mu\text{mol L}^{-1}$ ) in BW			
median	13.2	12.8	16.4	13.3	18.0	6.3	6.1	14.9
mean	20.4	16.1	15.8	16.9	18.6	11.8	6.6	17.3
max	59.6	44.5	19.3	39.3	32.9	43.2	11.4	39.8
min	5.4	2.0	10.2	5.4	4.8	2.7	2.7	2.0
n	11	57	4	8	11	57	4	8
Statistic	DOC $EF_{SML}$				POC $EF_{SML}$			
median <sup>a</sup>	1.35	1.53	1.37	1.51	1.83	2.25	1.52	1.98
mean <sup>a</sup>	1.36	1.93	1.30	1.99	1.88	2.51	1.42	1.95
min	0.99	0.20	0.76	0.80	0.44	0.20	0.20	0.20
max	1.68	9.09	1.79	5.25	3.96	12.9	2.53	5.06
n	10	54	4	7	10	54	4	8
Variable	Wind speed and chl-a categories							
wind	low	high	low	high	low	high	low	high
chl-a	low	low	high	high	low	low	high	high

<sup>a</sup> The median and mean enrichment factors were calculated from the data pairs listed in Table S1.

However, during high wind and periods characterized by high chl-a values, the concentrations in the SML were significantly higher than those in bulk water ( $p < 0.05$ ).

For POC, during time periods characterized by high chl-a concentrations and low wind speeds, concentrations detected in the SML are slightly higher than those observed in the bulk water ( $p = 0.02$ ). Despite the high variability of the data, no further significant differences between POC concentrations in the SML and bulk water were found for the other respective conditions. Occasionally, however, high POC and DOC concentrations occurred at low chl-a concentrations (**Figures 2 and 3**). These high concentrations point to an organic matter source not represented by chl-a concentration.

A comparison of the enrichment factors ( $EF_{SML}$ ) for DOC with POC based on different wind and chl-a

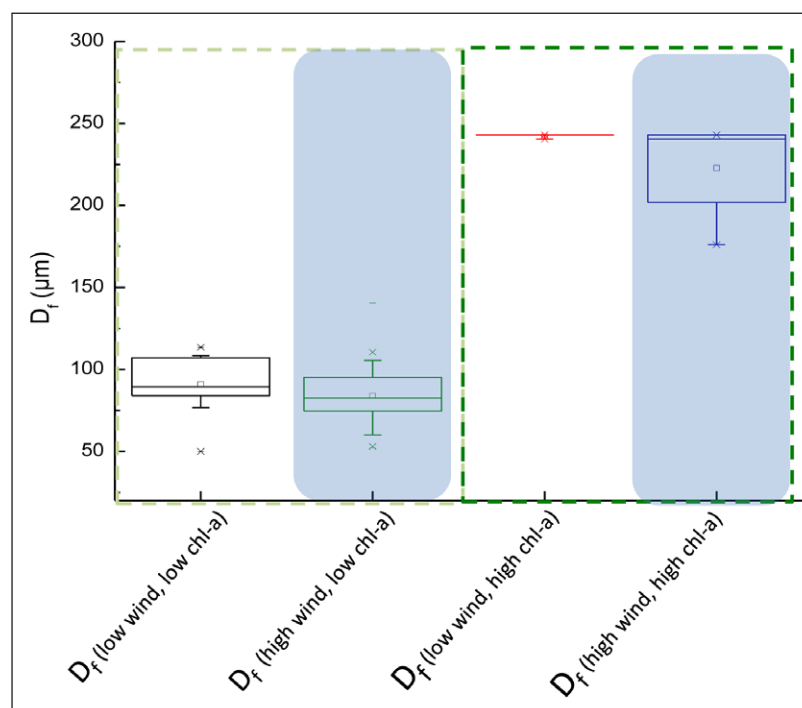
conditions shows that enrichment was consistently higher than 1 (**Table 3** and Figure S2). However, the enrichment did not differ significantly among the investigated categories. For high wind speeds, however, maximum EFs were consistently higher than 5, indicating a higher dynamic at high wind stress.

### 3.1.3 SML thickness

The thickness of the SML ( $D_f$ ) was determined according to Equation 4 and is shown in **Table 4** and **Figure 4**. To date, no uniform standard procedure exists for SML sampling, and the SML thickness data in this study are based on an operational definition that is certainly dependent on the applied sampling strategy. A valuable contribution to allow representative and standardized SML sampling has been achieved by Cunliffe and Wurl (2014). They

**Table 4:** Film thickness ( $D_f$ ) of the SML, according to different wind speed and chl-a categories. DOI: <https://doi.org/10.1525/elementa.225.t4>

Statistic	$D_f$ ( $\mu\text{m}$ )			
median	89.4	82.1	243	237
mean	91.0	83.0	242	209
min	50	52.0	241	91.8
max	114	111	243	243
n	11	57	3	8
Variable	Wind speed and chl-a categories			
wind	low	high	low	high
chl-a	low	low	high	high



**Figure 4: Film thickness of the SML.** Box and whisker plot of the film thickness ( $D_f$ ) of the SML. Each box encloses 50% of the data with the mean value represented as an open square and the median value represented as a line. The bottom of the box marks the 25% limit of the data, while the top marks the 75% limit. The lines extending from the top and bottom of each box are the 5% and 95% percentiles within the data set, while the asterisks indicate the data points lying outside of this range ("outliers"). The light green dashed lines encompass data from locations with low chl-a concentrations; the dark green dashed lines, those from locations with high chl-a concentrations. The solid blue fields highlight high wind speeds. DOI: <https://doi.org/10.1525/elementa.225.f4>

published a “guide to best practices to study the ocean’s surface” and reviewed current SML sampling strategies in order to provide best sampling protocols and create a consensus definition of the SML. In all campaigns of the present work, the same glass plate device and a uniform withdrawal rate of  $10 \text{ cm s}^{-1}$  were applied. Hence, among the campaigns, data are comparable. The median thickness of the SML at low chl-a concentrations was determined to be approximately  $80 \mu\text{m}$ , which closely corresponds to findings reported by Zhang et al. (2003), who demonstrated in the context of experiments that the typical SML thickness lies at approximately  $60 \mu\text{m}$ . During the Bergen campaign, characterized by a time period of high chl-a conditions, a much thicker SML was observed, with a mean thickness of  $230 \mu\text{m}$ . The sea surface temperature (SST) in Bergen was much lower ( $11^\circ\text{C}$ ) when compared to the other investigated regions (Table S1). Despite the fact that no clear correlation between SST and SML thickness was found for the different campaigns (Figure S3), the low SST values coincided with the high chl-a levels detected in Bergen (Pearson coefficient =  $-0.6$ ; **Table 2**). The cold waters tend to be more nutrient-rich, and phytoplankton more abundant, compared to warm waters (see, e.g., global maps of chl-a concentration and SST on <http://earthobservatory.nasa.gov/>, 29.11.16). The greater thickness of the SML sampled during the Bergen campaign can be taken to indicate an influence of oceanic biological activity on SML thickness, consistent with Galgani and Engel (2013) who demonstrated that enrichment of organic matter can enhance the SML thickness. However, in the present data set this difference in thickness is not reflected in either the EF or the concentration of the (bulk) organic parameters. A much thicker surface film was observed without detecting, correspondingly, a higher enrichment of DOC or POC in the sampled film when compared to the other regions. Surface-active compounds are likely to be enriched in the SML at high chl-a conditions, as previous work has shown that marine gel particles such as transparent exopolymer particles (TEP) and surfactants such as amino acids and fatty acids are strongly enriched there (Wurl et al., 2011a; Engel and Galgani, 2016). Such compounds, however, represent only a portion of DOC and POC; hence, variations in their concentrations and enrichment may not be reflected in the bulk parameters (e.g., van Pinxteren et al., 2012). A more detailed study on the nature of DOC and POC appears to be required in order to further investigate the impact of specific compound groups on the SML thickness.

Overall, the parameters POC and DOC were often found to be enriched, while concentration differences between SML and bulk seawater were relatively small; i.e., the enrichment factor was not high. POC was not significantly more enriched than DOC. Less enrichment was observed when concentrations were higher, which may be due to a sea-surface saturation effect. At high wind speeds, a higher variability of EFs occurred: i.e., higher maximum values were observed. At high chl-a conditions only slight differences in DOC and POC concentrations between SML and bulk water were detected. Although the SML thickness was significantly increased at high chl-a conditions, strong dependencies of DOC and POC concentrations and

enrichment on wind conditions and chl-a concentrations were not observed.

### 3.2 Aerosol particles

#### 3.2.1 Organic parameters WSOC and WISOC

Submicron aerosol particles ( $\text{PM}_{10}$ ) were sampled at all areas listed in **Table 1**. Similar to seawater and SML measurements, OC was distinguished into a water-soluble part (WSOC) and a water-insoluble part (WISOC). To ensure that measured aerosol particles would be of marine origin, only samples showing EC concentrations  $\leq 70 \text{ ng m}^{-3}$ , and therefore below the maximal EC concentration reported for clean marine air (Cavalli et al., 2004), as well as those from locations with air masses predominantly originating from the ocean (residence time index over water/ice  $> 0.7$ ; van Pinxteren et al., 2010), were considered in this study. Therefore, approximately 90% of the sampled aerosol filters utilized at the CVAO, but only 20% (*Polarstern* ANT-XXIX/10 2014) and 50% (*Polarstern* ANT-XXVIII/5 2012) of the filters applied during the ship cruises and 40% of the filters obtained during the Bergen campaign could be included in the interpretation. For the selected aerosol particles, no correlation between EC and WSOC or WISOC was observed. This lack of correlation served as a further confirmation that the influence of anthropogenic sources is of minor importance (Rinaldi et al., 2013). The observed concentrations of the main inorganic ions were quite similar across the different campaigns, falling within the ranges reported to indicate clean marine aerosol particles. Sulfate concentrations were observed to be between  $0.42$  and  $0.73 \mu\text{g m}^{-3}$ , which is in good agreement with concentration values reported for the remote tropical region (e.g., Müller et al., 2010). Sodium and magnesium correlated very well ( $R^2 = 0.78$ ) and nitrate concentrations were between  $0.02$  and  $0.05 \mu\text{g m}^{-3}$ . The molar ratio of  $\text{Cl}^-$  to  $\text{Na}^+$  was between  $0.34$  and  $0.76$  for the different campaigns and a lower  $\text{Cl}^-/\text{Na}^+$  ratio appeared to be mostly connected to a higher sulfate concentration (Figure S4). This connection could point to gas phase reactions (“aging”) of the particles resulting in a depletion of chloride and acidification of the particles. However, acidification of sea spray particles occurs in the timescale of seconds (e.g., Keene et al., 2007). Recently, Miyazaki et al. (2016) found a molar ratio of  $\text{Cl}^-/\text{Na}^+$  between  $1.06$  and  $0.32$  during different parts of a cruise in the Pacific Ocean. Nevertheless, based on isotopic carbon measurements, they found that the natural sources of the aerosol particles (regarding WSOC) were dominant during the entire cruise. Further detailed chemical investigations (e.g., products of gas phase reactions) would be required to study atmospheric processing (“aging”) of the particles. Based on the qualities of low EC, air masses of marine origin, and similar and overall low concentrations of inorganic ions across campaigns, the aerosol data reported in this study were considered to represent natural marine aerosol particles with minor contribution of anthropogenic sources. In the future, however, we plan to further confirm the “clean marine aerosol” classification by additional methods such as isotopic carbon measurements (e.g., Ceburnis et al., 2011).

WSOC concentrations of approximately  $0.2 (\pm 0.12, n = 64) \mu\text{g m}^{-3}$  were detected, therefore falling within the range of previously reported marine aerosol concentrations (e.g., by Cavalli et al., 2004). WISOC concentrations showed a higher variance with concentrations between  $0.01$  and  $0.9 \mu\text{g m}^{-3}$ . During some periods, the high WISOC concentrations appeared to correspond to low EC concentrations between  $10$  and  $30 \text{ ng m}^{-3}$ . An overview about organic aerosol concentrations in clean marine air has been published by Gantt and Meskhidze (2013). The concentrations of the present work fit well with the compilation of Gantt and Meskhidze (2013); however, in most of the studies no differentiation was made between WSOC and WISOC. Cavalli et al. (2004) summarized WISOC concentrations of the Mace Head region and reported WISOC values that averaged  $0.66 \mu\text{g m}^{-3}$ . At the same location, very high organic marine aerosol concentrations, peaking at  $3.8 \mu\text{g m}^{-3}$  during moderate wind speeds, have been reported by Ovadnaite et al. (2011) using aerosol mass spectrometry (measuring  $\text{PM}_{10}$  aerosol particles). These concentrations are much higher than determined with offline techniques, and they comprised 77% of the total submicron non-refractory mass. The pattern of the organic mass also revealed a unique marine fingerprint (Ovadnaite et al., 2011). O'Dowd et al. (2015) had reported previously high ambient submicron organic matter concentration (measured with aerosol mass spectrometry) exceeding  $4 \mu\text{g m}^{-3}$  at the Mace Head station during blooms. These aerosol organic matter concentrations measured with online techniques are not directly comparable to the offline method applied in the present work because with time-averaged offline sampling such high plumes cannot be captured. Nevertheless, the measured concentrations suggest a far stronger source of primary organic matter in marine air than assumed.

Regarding all aerosol data in this study, no significant correlation between WSOC and WISOC concentrations

was found. In addition, no correlation of WSOC or WISOC concentrations to wind speed could be observed over the sampling time of 24 hours, nor was a significant correlation apparent between chl-a concentration, serving as an indicator of seawater biological activity, and WSOC concentration. However, a connection between measured chl-a and WISOC concentrations was observed (Pearson coefficient = 0.64; **Table 2**).

### 3.2.2 WSOC and WISOC in relation to wind and chl-a categories

As for procedures applied to seawater, the obtained WSOC and WISOC data were classified into groups according to differing biological and meteorological conditions. The results are presented in **Table 5** and **Figure 5**. Compared to the results obtained for DOC and POC concentrations in seawater, wind and chl-a conditions generally had a stronger impact on WSOC and WISOC concentrations sampled on aerosol particles. Differences in concentration values at low chl-a conditions were minor.

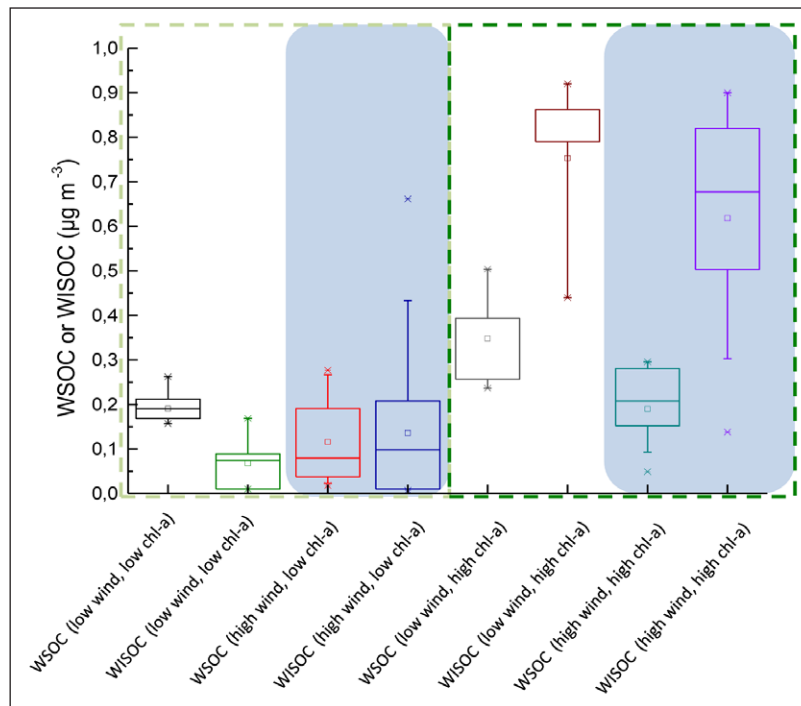
During the Bergen campaign that was shaped by high chl-a concentrations, concentrations of both WSOC and WISOC were higher and showed greater variance, and WISOC concentrations were significantly higher than WSOC ( $p < 0.05$ ; compare box plots in the high chl-a section of **Figure 5**). On average, WSOC was higher by 30% and WISOC by 85% compared to periods shaped by low chl-a concentrations. Furthermore, approximately 60% more WISOC than WSOC was present on the aerosol particles. That contamination from terrestrial sources may have biased the data cannot be ruled out completely. However, the application of the “clean marine air” criteria suggested that only a minor contribution may have derived from anthropogenic sources. Besides chl-a concentrations, the WISOC was also connected to SML thickness (Pearson coefficient = 0.61; **Table 2**). The high WISOC concentrations are likely caused by an oceanic bubble

**Table 5:** Concentrations of water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WISOC) in submicron aerosol particles ( $\text{PM}_{10}$ ) and enrichment factors of DOC and POC in  $\text{PM}_{10}$  ( $\text{EF}_{\text{aer}}$ ), according to different wind speed and chl-a categories. DOI: <https://doi.org/10.1525/elementa.225.t5>

Statistic	WSOC ( $\mu\text{g m}^{-3}$ ) in $\text{PM}_{10}$				WISOC ( $\mu\text{g m}^{-3}$ ) in $\text{PM}_{10}$			
median	0.18	0.16	0.33	0.21	0.04	0.10	0.83	0.68
mean	0.19	0.17	0.35	0.19	0.07	0.14	0.75	0.62
max	0.26	0.64	0.50	0.30	0.17	0.66	0.92	0.90
min	0.16	0.01	0.24	0.05	0.01	0.01	0.44	0.14
n	10	39	4	11	8	37	4	11
Statistic	$\text{EF}_{\text{aer}}$ (DOC) <sup>a</sup>				$\text{EF}_{\text{aer}}$ (POC) <sup>a</sup>			
median	$1.1 \times 10^4$	$1.5 \times 10^4$	$3.4 \times 10^4$	$1.2 \times 10^4$	$6.4 \times 10^3$	$9.0 \times 10^4$	$6.6 \times 10^5$	$5.7 \times 10^5$
mean	$1.5 \times 10^4$	$1.8 \times 10^4$	–	–	$2.1 \times 10^4$	$1.8 \times 10^5$	–	–
max	$4.0 \times 10^4$	$6.4 \times 10^4$	–	–	$8.6 \times 10^4$	$9.8 \times 10^5$	–	–
min	$4.4 \times 10^3$	$6.4 \times 10^1$	–	–	$1.8 \times 10^3$	$3.3 \times 10^3$	–	–
n	6	35	1	1	5	31	1	1
Variable	Wind speed and chl-a categories							
wind	low	high	low	high	low	high	low	high
chl-a	low	low	high	high	low	low	high	high

<sup>a</sup>  $\text{EF}_{\text{aer}}$  were calculated based on combinations of daily samples of SML and aerosol sampling events (see text for details).





**Figure 5: Concentrations of WSOC and WISOC.** Box and whisker plot of the concentrations of water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WISOC) found on aerosol particles. Each box encloses 50% of the data with the mean value represented as an open square and the median value represented as a line. The bottom of the box marks the 25% limit of the data, while the top marks the 75% limit. The lines extending from the top and bottom of each box are the 5% and 95% percentiles within the data set, while the asterisks indicate the data points lying outside of this range (“outliers”). Boxes are color-coded to indicate paired samplings of WSOC and WISOC. The light green dashed lines encompass data from locations with low chl-a concentrations; the dark green dashed lines, those from locations with high chl-a concentrations. The solid blue fields highlight data from locations with high wind speeds. DOI: <https://doi.org/10.1525/elementa.225.f5>

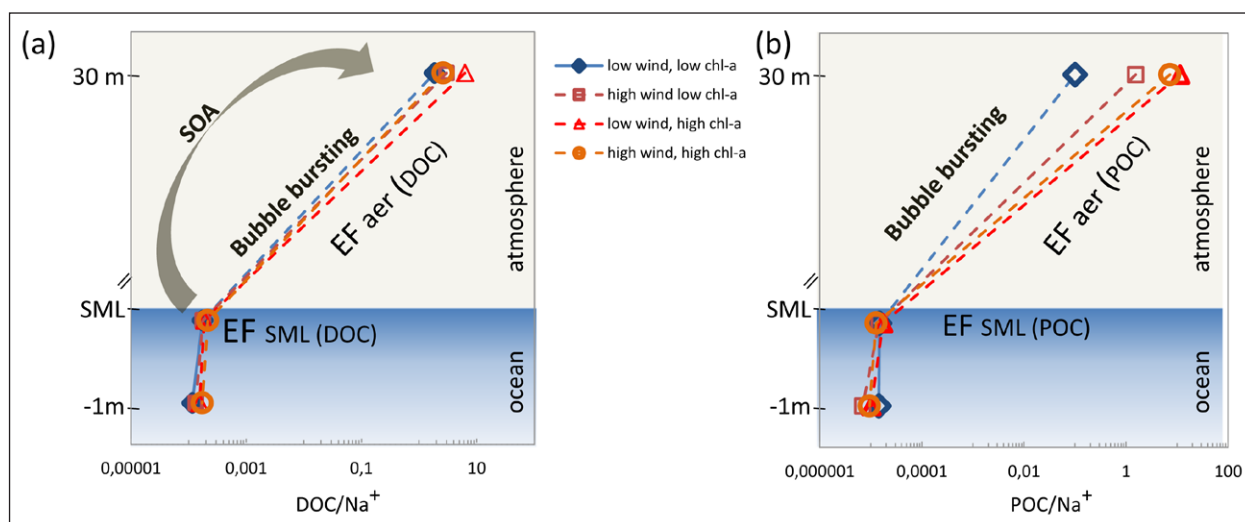
bursting source, as also previously reported (Ceburnis et al., 2008; Facchini et al., 2008b), and seem to be additionally affected by biological activity in the ocean. High WISOC concentrations occurring even at low wind speeds suggest that wind intensity above the oceans is consistently sufficient for organic matter to be transferred from the oceans to the atmosphere. However, besides wind, other sources have been identified that may be responsible for the transfer of organic matter from the ocean to the atmosphere, as previously observed, for example, in the Arctic at low wind speeds (Leck et al., 2002). Bubbles can be formed as a result of processes such as microbial respiration (Johnson and Wangersky, 1987), presenting an additional transfer possibility for organic matter – predominantly at time periods characterized by high biological activity, such as during the Bergen campaign. WSOC concentrations can in part be attributed to other (secondary) sources and may therefore not be as strongly affected by oceanic biological activity as WISOC.

### 3.3 Enrichment factors in submicron aerosol particles ( $EF_{aer}$ )

As a next step, the organic carbon concentrations detected in the SML and on the aerosol particles were considered in relation to each other. Seawater and aerosol samples were taken simultaneously, and only clean marine air masses were considered (see Section 3.2.1). At the CVAO,

for example, the air masses were demonstrated to follow the water current (Figure S5), enhancing the organic carbon link between the SML and the aerosol particles. As mainly winds drive the ocean currents in the upper 100 m of the ocean, there is a likely connection between organic carbon on aerosol particles and organic carbon observed in the SML.

To compare organic carbon concentrations found in seawater and aerosol particles, enrichment factors of the organic carbon on the submicron aerosol particles ( $EF_{aer}$ ) were determined by relating the WSOC (WISOC) observed in the aerosol particles and the DOC (POC) found in the SML to sodium as a conservative tracer for sea salt (e.g., Sander et al., 2003; Keene et al., 2007; Russell et al., 2010) applying Equations 5 and 6. Overall, the  $EF_{aer}$  (DOC) is about  $10^4$  and the  $EF_{aer}$  (POC) is about  $10^5$  (Table 5, Figure S6). These data represent the first  $EF_{aer}$  (DOC) and  $EF_{aer}$  (POC) obtained on the basis of concerted measurements, i.e., from simultaneous measurements of the SML and submicron aerosol particles in the marine environment. Figure 6 illustrates that the enrichment of DOC and POC detected in the aerosol particles is orders of magnitude higher than the enrichment of DOC and POC in the SML. The concentrations of DOC and POC detected in the SML, however, are strongly dependent on the thickness of the SML sampled and thus the sampling technique. By use of the described sampling method involving a glass



**Figure 6: The enrichment of DOC and POC in the SML and in aerosol particles.** Comparison of the seawater and aerosol ratios of DOC (WSOC) to sodium ( $\text{Na}^+$ ) **(a)** and POC (WISOC) to  $\text{Na}^+$  **(b)** to illustrate their enrichments in SML and aerosol particles at different wind and chl-a conditions. The secondary organic aerosol (SOA) arrow in (a) illustrates that additional DOC originating from the gas phase is likely to contribute to the concentrations measured on aerosol particles. DOI: <https://doi.org/10.1525/elementa.225.f6>

plate, SML thicknesses of 83–242  $\mu\text{m}$  were determined (Table 4). It is likely that the thinner the sampled SML, the higher the  $\text{DOC}/\text{Na}$  and  $\text{POC}/\text{Na}$  ratios, so that methods yielding thinner SML samples would result in smaller  $\text{EF}_{\text{aer}}$  for DOC and POC.

Data reported in the literature for enrichment factors of organic carbon in aerosol particles have been obtained mostly in the context of laboratory experiments, often utilizing natural seawater with an artificial bubbling apparatus. As the enrichment factors for organic carbon are often reported as a total sum (without distinguishing between DOC and POC), they are designated as  $\text{EF}_{\text{aer}}(\text{OC})$  in the following discussion. Based on artificial bubbling experiments,  $\text{EF}_{\text{aer}}(\text{OC})$  values ranging between  $10^3$  and  $10^4$  but also values up to  $10^5$  have been reported (Quinn et al., 2015, and references therein). Only one study reports  $\text{EF}_{\text{aer}}(\text{OC})$  values for ambient marine aerosol particles, with maximal values of about  $10^3$  (Russell et al., 2010). These authors measured organic carbon on aerosol particles and combined them with data on organic carbon in seawater from the literature. Given the range of published  $\text{EF}_{\text{aer}}(\text{OC})$  values, the  $\text{EF}_{\text{aer}}(\text{DOC})$  and the  $\text{EF}_{\text{aer}}(\text{POC})$  values in the present study (Table 5), based on ambient marine measurements, are located at the upper end.

The results presented in Figure 6 and Table 5 demonstrate that the  $\text{EF}_{\text{aer}}(\text{DOC})$  values are quite uniform ( $10^4$ ), independent of the different wind and chl-a conditions. As mentioned in the introduction, DOC can be transferred to aerosol particles via bubble bursting and via secondary production by gas-to-particle conversion (secondary organic aerosol, SOA). The contribution of SOA in the marine atmosphere, however, is highly uncertain according to a recent review, and probably significantly smaller than the direct or primary transfer mechanism via bubble bursting (Quinn et al., 2015, and references therein). From the data here, we cannot differentiate between primary and secondary sources for the WSOC on the aerosol

particles and therefore indicated the additional SOA processes in Figure 6. However, the transfer of POC to WISOC is naturally related to primary, bubble bursting transfer processes. The  $\text{EF}_{\text{aer}}(\text{POC})$  values, as a result of POC and WISOC concentrations, exhibit a greater variability and are significantly higher at high chl-a conditions. Highest enrichment values of organic matter in aerosol particles occurring when biological activity is also high has been reported previously (O'Dowd et al., 2004; Facchini et al., 2008b). However, in other studies of mainly oligotrophic areas, such a correlation between organic matter on aerosol particles and chl-a concentration could not be observed (Russell et al., 2010; Quinn et al., 2014). Some studies report high organic aerosol concentrations in connection to dimethylsulfide (Bates et al., 2012) or to heterotrophic bacteria (Prather et al., 2013) rather than to chl-a conditions. The  $\text{EF}_{\text{aer}}(\text{POC})$  values obtained during this study support the hypothesis that organic carbon enrichment in marine aerosol particles is coupled to oceanic biological activity represented by chl-a conditions.

In general, on the basis of the results reported here, no strong fluctuations in bulk water and SML concentrations or in the SML enrichment of DOC and POC at different wind speeds and chl-a conditions were observed. WSOC and WISOC concentrations in the aerosol particles, however, were significantly affected by elevated chl-a concentrations. These findings, along with very high and highly variable values for  $\text{EF}_{\text{aer}}(\text{DOC})$  and  $\text{EF}_{\text{aer}}(\text{POC})$ , suggest that processes within the water column selectively transport organic carbon from the bulk water to the SML and subsequently from the ocean surface into the atmosphere. Such transfer processes have been studied in detail by Schmitt-Kopplin et al. (2012), who reported a vertical enrichment of biomolecules (such as functionalized fatty acids, monoterpenes and sugars) from the surface ocean into the atmosphere by bubble-mediated processes. The surface-active molecules are

selectively transported from the surface water to the bubble interface and then into the aerosol phase via sea spray. The authors concluded that there is a chemo-selective transfer of natural organic compounds from seawater to atmosphere.

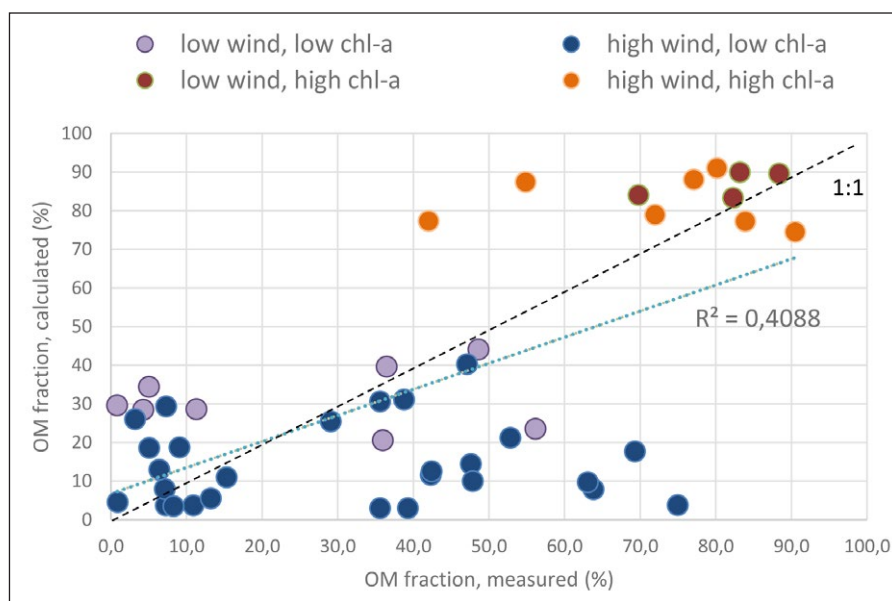
More specifically, Frossard et al. (2014) found that the organic composition of aerosol particles changed while bubbling oligotrophic versus eutrophic seawater, although the average composition of seawater OM remained fairly similar. These authors suggested that the presence of a thick SML at high biological activity stabilizes the bubble film and increases bubble persistence at the seawater surface. The longer the bubbles persist, the more they potentially drain. This increase in bubble persistence time leads to a drainage of more soluble compounds, leaving the less soluble compounds enriched on the bubbles. The end result is the presence of bubble films and primary aerosol particles with a larger fraction of non-soluble compounds (Frossard et al., 2014).

The findings of the present study – that more WISOC (less soluble compounds) are present on aerosol particles at high biological activity while the seawater concentrations do not differ significantly – agree with the observations described by Frossard et al. (2014). They indicate the involvement of different transport mechanisms depending on the level of oceanic biological activity. Furthermore, the low SST registered in Bergen (compared to the other investigated regions) may also affect the organic transfer processes, as bubble bursting processes are suggested to be influenced by the SST (Lewis and Schwartz, 2004). In the future, more systematic laboratory studies are needed in order to elucidate the transfer of organic carbon with its different chemical

compound classes with emphasis on clarifying the role of bubble interfaces against direct transfer from the SML.

### 3.4 Implementation of $OM_{SSA}$ in a source function based on wind speed and chl-a conditions

Rinaldi et al. (2013) presented a source function for the prediction of sea spray organic matter ( $OM_{SSA}$ ) in  $PM_{10}$  based on chl-a conditions and wind speed. This source function was developed for use at the Mace Head station at the easterly rim of the North Atlantic Ocean. As the present measurements were conducted in the Atlantic Ocean, with the majority located in the Northern hemisphere, these measurements were compared with the source function. First, the  $OM_{SSA}$  fraction was calculated on the basis of the WISOC measurements (as shown in Figure S7), based on the assumption that primary marine organic matter is primarily water-insoluble (Rinaldi et al., 2013). The  $OM_{SSA}$  fractions are highly variable with fractions up to 90% in the productive region of Bergen. These fractions are much higher than the low and constant (around 10%)  $OM_{SSA}$  fractions reported by Quinn et al. (2015) in northwestern Atlantic and Pacific waters. Model calculations report overall organic fractions of submicron sea spray in the range of 0.5 to 0.7 over blooming regions (Burrows et al., 2016). However, at the Mace Head station in the north-eastern Atlantic Ocean (regionally close to Bergen), Rinaldi et al. (2013) observed a maximum  $OM_{SSA}$  fraction of 78%, and O'Dowd et al. (2015) reported that  $OM_{SSA}$  fractions can reach up to 95% of submicron mass. The comparison of the measured and the predicted  $OM_{SSA}$  fractions is illustrated in **Figure 7**. It shows an apparent large scattering for low  $OM_{SSA}$  fractions, while better agreement is achieved



**Figure 7: Calculated and measured organic mass fractions ( $OM_{SSA}$ ).** Scatter plot showing the relation between measured WISOC concentrations (transferred to  $OM_{SSA}$ ) and the calculated  $OM_{SSA}$  according to the parameterization by Rinaldi et al. (2013) using chl-a concentrations and wind speed conditions as input parameters. The applied equation from Rinaldi et al. (2013) is ( $R = 0.82$ ):  $OM_{SSA} = (56.9 \times \text{chl-a}) + (-4.64 \times \text{wind speed}) + 40.9$ . DOI: <https://doi.org/10.1525/elementa.225.f7>

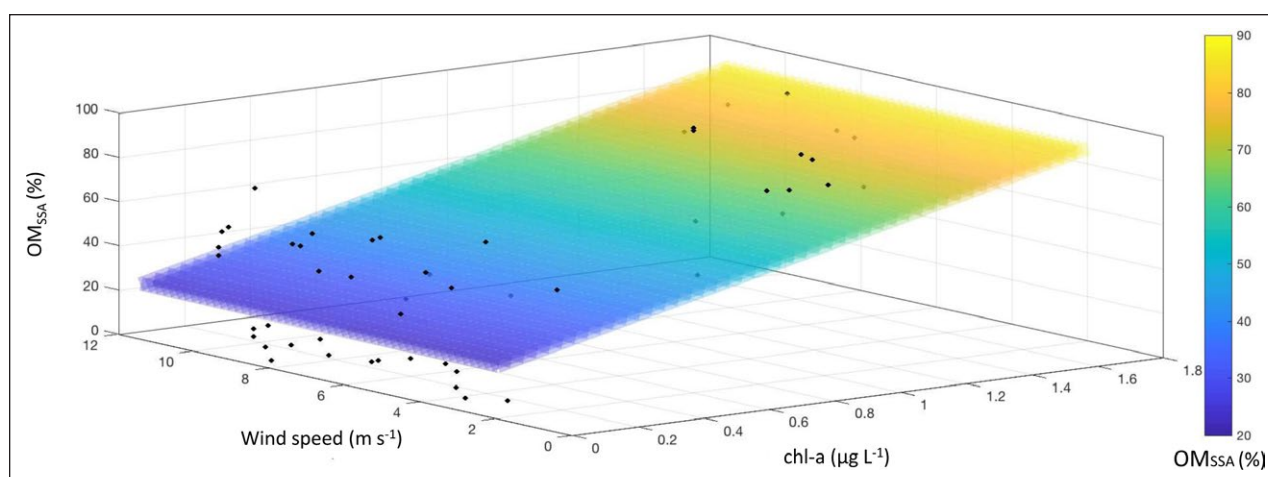
for high  $OM_{SSA}$  fractions at elevated chl-a values. A strong underestimation of calculated  $OM_{SSA}$  (approximately 30%) is found under conditions characterized by low chl-a concentrations and high wind speeds. Rinaldi et al. (2013) were able to improve the source function by using chl-a data with a time lag of one week between the chl-a and the particle  $OM_{SSA}$  determinations. O'Dowd et al. (2015) also recently suggested that large quantities of transferable organic carbon are released during the decay phase of the bloom. However, the application of chl-a data with a time delay of seven days to the present measurements led to an even greater underestimation of  $OM_{SSA}$  in the high  $OM_{SSA}$  range (Figure S8). A time delay was therefore not applied to the present data. Altogether, it appears that the source function yields good results for time periods characterized by high degrees of biological activity, but fails to predict  $OM_{SSA}$  in oligotrophic regions, especially at high wind speeds.

As a next step, the issue of whether a variation of the parameters of the source function would result in a better description of the  $OM_{SSA}$  in relation to wind speed and chl-a concentrations was investigated. To this end, several two-dimensional regression approaches were tested. The large scatter of the data, however, especially in the low chl-a concentration range, could not be represented properly in the different applied source functions. The best and quite simple function was based on a linear regression, with  $R^2 = 0.48$ :

$$OM_{SSA} = 23.64 + (35.25 \times \text{chl-a}) + (0.11 \times \text{wind speed}). \quad (7)$$

Once again, the results (Figure 8) clearly reveal that  $OM_{SSA}$  levels are at their highest at elevated chl-a conditions ( $OM_{SSA}$  median: 78%), which is in good agreement with Rinaldi et al. (2013). However, at low chl-a conditions, the  $OM_{SSA}$  levels occur in two distinct fractions: a

medium ( $OM_{SSA}$  median: 42%) and a low ( $OM_{SSA}$  median: 7%) fraction. The low  $OM_{SSA}$  fractions are again in good agreement with the results of the source function from Rinaldi et al. (2013). However, the medium  $OM_{SSA}$  fractions are not in good agreement with the source function and apparently cannot be represented by chl-a and wind speed exclusively. This result suggests the presence of an additional  $OM_{SSA}$  source during oligotrophic conditions. This additional source could either be biological – where chl-a, however, does not serve as an indicator – or possibly of a different nature. As mentioned in Section 3.3, other authors have observed high organic aerosol concentrations in connection to dimethylsulfide (Bates et al., 2012) or to heterotrophic bacteria (Prather et al., 2013). The medium  $OM_{SSA}$  fractions were mainly found in the region of the Cape Verde islands (campaigns: November 2011 and 2013) under remote marine conditions, with chl-a concentrations around  $0.2 \mu\text{g L}^{-1}$  and wind speeds of  $7.6 \text{ m s}^{-1}$  on average. Of particular interest to our future investigations will be a closer inspection of the nature of the medium  $OM_{SSA}$  fraction in oligotrophic regions. Regarding the impact of wind speed, Rinaldi et al. (2013) and Gantt et al. (2011) predicted that the highest organic enrichment in sea spray aerosol particles will occur during calm winds when the ocean surface is strongly covered by the SML. Gantt et al. (2011) demonstrated that at higher wind speeds (up to  $8 \text{ m s}^{-1}$ ), the sea spray production is elevated, whereas  $OM_{SSA}$  in aerosol particles is reduced due to the stronger mixing of SML with bulk water and the corresponding lower SML coverage. Based on the WSOC and WISOC measurements as well as the  $OM_{SSA}$  fraction (Figure S7) obtained in this study, no inverse relation between  $OM_{SSA}$  fraction and wind speed could be observed. Generally, the biological activity of the ocean, as reflected by chl-a conditions, had a significantly higher impact on OC transfer from seawater onto aerosol



**Figure 8: Plot of the  $OM_{SSA}$  source function.** Plot of the two-dimensional regression analysis for  $OM_{SSA}$  based on chl-a concentrations and wind speed. Function of best fit ( $R^2 = 0.48$ ):  $OM_{SSA} = 23.64 + (35.25 \times \text{chl-a}) + (0.11 \times \text{wind speed})$ . The upper limit of  $OM_{SSA}$  in the source function was set to 91% (corresponding to the maximum  $OM_{SSA}$  values observed), while the lower limit was set to 0%, as some combinations of chl-a levels and wind speed lead to negative  $OM_{SSA}$  values. The color bar indicates %  $OM_{SSA}$ ; the graph clearly illustrates a threefold division of the  $OM_{SSA}$  fractions: high  $OM_{SSA}$  ( $OM_{SSA}$  median: 78%) at high chl-a conditions, and medium  $OM_{SSA}$  ( $OM_{SSA}$  median: 42%) and low  $OM_{SSA}$  ( $OM_{SSA}$  median: 7%) at low chl-a conditions. DOI: <https://doi.org/10.1525/elementa.225.f8>



particles compared to wind speed. Source functions aimed at predicting the occurrence of organic matter on marine aerosol particles based solely on wind speed and chl-a concentration levels, however, should be taken with caution when investigating different regions of the Atlantic Ocean. Certainly, other meteorological parameters besides wind speed, as well as biological parameters beyond chl-a concentration, affect organic matter on marine aerosol particles, especially in oligotrophic regions.

#### 4 Summary and conclusions

The results of measurements of DOC and POC concentrations and enrichment factors in the SML, as well as WSOC and WISOC measurements in marine aerosol particles, were presented. The concentrations of DOC and POC in seawater (bulk water and the SML) tended to be relatively uniform across the particular regions of the North and Central Atlantic Ocean. Organic carbon was enriched in the SML by a factor of two on average, following a pattern that may be explained by a surface saturation effect (higher enrichment at lower concentrations). The impact of different wind speeds and varying degrees of biological activity, as indicated by chl-a concentration levels, on DOC and POC concentrations as well as enrichment factors were observed to be minor. However, a thicker surface film was observed at elevated chl-a concentration levels, which may be due to surface-active species assumed to represent only a small fraction of DOC and POC. In contrast to organic carbon measured in seawater, the organic carbon levels observed in aerosol particles were significantly affected by varying levels of chl-a.

On the basis of the present ambient concerted measurements, enrichment factors for DOC and POC in ambient marine aerosol particles, hitherto not reported in the literature, were obtained. These enrichment factors fall at the upper end of the range of values reported in the framework of experimental studies using artificial bubbling devices in the laboratory and in the field. This finding indicates that the transfer of organic carbon from the SML into the aerosol phase in the real-world marine environment is consistent with processes described in laboratory studies.

The results obtained in the present study support the thesis that elevated local biological activity (as indicated by chl-a concentrations) enhances (primary) organic carbon concentration on aerosol particles. These field results furthermore support the thesis of a chemo-selective transfer of organic compound groups, which has been reported in the framework of studies using artificial bubbling devices. However, a prediction of the WISOC measurement results (transferred to  $OM_{SSA}$ ) by source functions based on wind speed and chl-a levels showed a strong underestimation of  $OM_{SSA}$  in oligotrophic regions, especially at high wind speeds. For the North and Central Atlantic Ocean there may be additional parameters – either connected to biological factors not served by chl-a level as an indicator or to factors of a different nature – that must be taken into consideration in order to accurately predict the organic fractions on aerosol particles.

In the future, a more detailed investigation of the chemical nature of DOC and POC in seawater and aerosol particles is required in order to identify suitable tracers for primary and secondary organic aerosols. Moreover, a more comprehensive classification of “clean marine aerosol particles” is needed. Besides characterization of the chemical nature, isotopic analysis can help to differentiate marine and continental sources. In addition, further studies on suitable proxies for oceanic biological activity are needed to describe the organic composition of seawater. Burrows et al. (2014) recently introduced a new concept aimed at predicting the mass of organic matter in aerosol particles based on their different physical and chemical properties. Representative model compounds as suggested by Burrows et al. (2014) should be measured in ambient marine samples.

#### Data Accessibility Statement

The datasets will be available in the PANGAEA database.

#### Supplemental Files

The supplemental files for this article can be found as follows:

- **Figure S1.** Measured (LC-FLD) vs. satellite concentration of chlorophyll-a (chl-a) during all campaigns. DOI: <https://doi.org/10.1525/elementa.225.s1>
- **Figure S2.** Enrichment factors of DOC and POC in the SML. DOI: <https://doi.org/10.1525/elementa.225.s2>
- **Figure S3.** Water temperature vs. film thickness during the campaigns. DOI: <https://doi.org/10.1525/elementa.225.s3>
- **Figure S4.** Concentrations of the main inorganic ions during the different cruises. DOI: <https://doi.org/10.1525/elementa.225.s4>
- **Figure S5.** Air and water origin at the Cape Verde island Sao Vicente. DOI: <https://doi.org/10.1525/elementa.225.s5>
- **Figure S6.** The enrichment factors of DOC and POC in the aerosol particles. DOI: <https://doi.org/10.1525/elementa.225.s6>
- **Figure S7.** The  $OM_{SSA}$  fraction. DOI: <https://doi.org/10.1525/elementa.225.s7>
- **Figure S8.** Plot of the  $OM_{SSA}$  source function with one week-averaged chl-a values. DOI: <https://doi.org/10.1525/elementa.225.s8>
- **Table S1.** Concentrations of dissolved and particulate organic carbon (DOC, POC) in the sea surface microlayer (SML) and in bulk water (BW) and their enrichment factors (EF) together with chl-a concentrations and wind speed. DOI: <https://doi.org/10.1525/elementa.225.s9>
- **Table S2.** Concentrations of water soluble and water insoluble organic carbon organic carbon (WSOC, WISOC), elemental carbon (EC) and sodium ( $Na^+$ ) in the submicron aerosol particles together with together with chl-a concentrations and wind speed. DOI: <https://doi.org/10.1525/elementa.225.s10>

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## Competing interests

The authors have no competing interests to declare.

## Author contributions

- MvP and HH designed and organized the field campaigns.
- MvP, KWF and KM performed the field campaigns and contributed to the acquisition of the data.
- SB contributed to the regression analysis.
- WvT organized and conducted analysis of biological tracers.
- MvP and HH performed the data interpretation and wrote the paper with input from all authors.

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